

# PATENT SPECIFICATION

DRAWINGS ATTACHED

**L 102,771**

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## COMPLETE SPECIFICATION

### Preparation of Stereoregular Polyvinyl Alcohol Fibres or Filaments

We, MONSANTO COMPANY, of 800 North Lindbergh Boulevard, St. Louis, Missouri, United States of America, a corporation organized and existing under the Laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of fibers and filaments from polymers of stereoregular polyvinyl alcohol by the spinning of solutions of polyvinyl esters of halogenated acetic acids and the subsequent continuous conversion of the resulting filament or the like by hydrolysis to stereo-regular polyvinyl alcohol.

Polyvinyl alcohol has long been recognized as an attractive polymer well suited for the production of fibers and filaments. However, its wide utilization for this purpose has been hindered by its solubility in water. Various approaches have been used to circumvent this deficiency in polyvinyl alcohol. Initially, polyvinyl alcohol articles when unmodified are quite soluble in water and particularly in hot water so that they are totally unsuitable for use as textile fibers for the production of fabrics and garments which can be laundered or otherwise exposed to water. Subsequently, it was discovered that such polyvinyl alcohol filaments could be treated with agents such as aldehydes, particularly formaldehyde, which treatment results in an insoluble fiber in cold and hot water by partially cross-linking the polymer. However, the formaldehyde treatment resulted in a loss of many desirable characteristics of the initial polymer articles. They were rendered quite rough and stiff and the degree of cross-linking by the various agents had to be strictly controlled in order to produce fibers which were suitable for use in textile products. Furthermore, the addition of this cross-linking or post treating step in-

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volves additional factors of cost which rendered the articles produced from the polyvinyl alcohol polymers less attractive for commercial purposes. In addition to aldehyde treatment several other mutually related approaches to making polyvinyl alcohol fibers less sensitive to water have been investigated and reported. In general, common to these processes is the use of a highly hydrolized water soluble polyvinyl alcohol for spinning, the use of a separate hot draw step, and absence of a chemical after treatment. In each case fiber which is insoluble in boiling water is reported. In several of these processes polyvinyl alcohol derived from conventionally prepared polyvinyl acetate is employed. The other processes use polyvinyl alcohols derived from a polyvinyl acetate or a polyvinyl formate which has been prepared under special conditions. In all of these processes, however, the polyvinyl alcohol which is spun is more soluble than the fiber obtained. Although some of the polymers used in these processes are undoubtedly marginally different in structure from conventional polyvinyl alcohols, the success of the process in every case is apparently the result of a hot drawing step. Excellent ordering of the molecules in the fiber appears to be the real key to the insolubility of the fibers produced. All fibers reported from such processes have elongations too low for many textile uses, with 10 percent elongation being a typical upper limit. This low elongation appears to be an inherent property of water insoluble fibers prepared from water soluble polymer.

Recently there has been reported the preparation of highly stereo-regular polyvinyl alcohol. This highly stereo-regular polymeric material, in contrast to the normal polyvinyl alcohol, is completely insoluble in both cold and hot water, including boiling water. The insolubility of stereo-regular polyvinyl alcohol in water at 100° C. has been attributed to the stereoregularity of the alcohol as contrasted

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to the non-stereoregular structure possessed by conventional polyvinyl alcohol. Unfortunately, however, the polymer is likewise insoluble in practically all known solvents. For this reason, no practical wet or dry spinning process has to date been developed at least on a commercial basis which employs the recently prepared highly stereoregular polyvinyl alcohol polymers. Furthermore, the stereoregular polyvinyl alcohol polymers do not melt without drastic decomposition, and therefore no process for melt extruding shaped articles from these polymers appears to be practical. Therefore, although an excellent material for the fabrication of fibers and filaments has now been developed, there still remains no practical commercial manner of forming such articles from these polymers.

The use of the term "stereoregular" herein refers to a particular characteristic of certain polymers which has become a well known phenomenon. Both the polyvinyl trihaloacetates and the derived polyvinyl alcohols are believed to have the syndiotactic type of stereoregularity.

The present invention provides a method for preparing filaments and fibers of highly stereoregular polyvinyl alcohol.

The invention also provides a wet spinning method for the preparation of filaments and fibers of stereoregular polyvinyl alcohol which is capable of successful commercial continuous spinning thereby producing suitable and saleable filaments and fibers for a wide range of uses.

According to the present invention a process for the preparation of boiling water insoluble stereoregular polyvinyl alcohol fibres or filaments, comprises wet or dry spinning a solution of a stereoregular polyvinyl ester of halogenated acetic acid, in which all three hydrogen atoms of the methyl group in the acetic acid have been substituted by either chlorine or fluorine or by both chlorine and fluorine and continuously hydrolyzing the resulting fibre or filament.

The hydrolysis may conveniently be carried out by means of a base having a  $pK_b$  value less than 8.0 ( $pK_b = -\log_{10}$  of  $K_b = \log_{10} \frac{1}{K_b}$  where  $K_b$  is the ionisation constant of the base) and thereafter drying and heat stretching the resulting stereoregular polyvinyl alcohol fibre or filament.

The fibres or filaments which are hydrolyzed are prepared from polymers of vinyl esters of halogenated acetic acid selected from monomeric compounds having the formula



wherein X is chlorine, fluorine or mixtures thereof. The vinyl esters of halogenated acetic acids which are suitable for the present in-

vention are vinyl trifluoroacetate, vinyl monochlorodifluoroacetate, vinyl dichloromono-fluoroacetate and vinyl trichloroacetate.

The highly stereoregular polymers of the vinyl esters of the halogenated acetic acids identified above can be produced by methods known in the art. Thus they may be produced by a free radical polymerization process at low temperatures employing free radical catalysts such as tri-n-butyl boron with or without other organic diluents such as heptane, cyclohexane, and so forth. Polymers with a lower degree of stereoregularity can be produced at temperatures above 0° C. by means of these catalysts. However, in order to obtain highly stereoregular polymers these polymerizations should be conducted at temperatures of from 0° C. to as low as about -95° C to -100° C. The degree of stereoregularity of the resulting polymers increases with lowering temperature. Preparation at -50° C to -78° C is preferred with no substantial differences in properties of polymer prepared in this range and those of polymer prepared at lower temperatures.

The spinning of the stereoregular polyvinyl esters of haloacetic acids may be accomplished by any of the well known wet or dry spinning methods. Any convenient solvent that will dissolve stereoregular polyvinyl esters of haloacetic acids is suitable for use in the spinning process. Useful solvents include organic liquids which contain oxygen in the form of ether or carbonyl. These solvents include acetone, methyl ethyl ketone, ethyl acetate, dimethylformamide, dimethylacetamide, cyclohexanone, tetrahydrofuran, methyl formate and the like.

In a preferred wet spinning process the coagulating bath can be any liquid which is a solvent for or is miscible with the solvent employed in the spinning solution but is a non-solvent for the polymer. Both polar and non-polar liquids may be employed but polar ones such as water are preferred.

Immediately after coagulation the fiber is subjected to a hot stretch prior to hydrolysis. This heat stretch operation involves a simultaneous wash stretch in the hot water bath. The fiber is subjected to a stretch at a stretch rate of from 1.05 to 8.0:1.0 while passing through the hot water bath.

At this point in the continuous process of the invention the fiber is now ready for the hydrolysis step whereby the fiber is converted to a polyvinyl alcohol fiber. As used herein the term "hydrolysis" includes any reaction whereby the polyvinyl ester of halogenated acetic acids are converted to polyvinyl alcohol. The hydrolysis is conveniently conducted by winding the fiber on a series of one or more godets which wet and hydrolyze the fibers while passing around the godets. The hydrolysis agent can be any base with a  $pK_b$  value less than 8.0. Such bases include ammo-

5 nium hydroxide, methanolic ammonia, primary amines such as methylamine, ethylamine, propylamine, butylamine, secondary amines such as piperidine, dimethylamine, diethylamine, dipropylamine, dibutylamine, methyl-ethylamine, quarternary amines such as tetra-  
10 n-butyl ammonium hydroxide, tetramethyl ammonium hydroxide and the like. The hydrolysis reaction is a continuous reaction usually requiring about 1 to 5 minutes, preferably 1 to 2 minutes.

15 The fiber while passing from the hydrolysis bath to the dryer rollers is held at constant length or subjected to a stretch of from about 1.05 to 3.0 draw ratio depending upon the amount of stretch already applied.

20 After hydrolysis and post-hydrolysis stretch the fiber is passed over a heated godet at a temperature of from 80° C. to 110° C. which substantially dries the fiber.

25 In order to obtain fiber of high tenacity an additional heat stretch step is used after the fiber has been dried. This involves drawing the fibre over a heated apparatus such as a hot pin or shoe at a temperature of from 95° C. to 200° C. while subjecting the fiber to a stretch of from about 1.1 to 5.0 draw ratio, preferably about 1.1 to 2.5 draw ratio. In general the higher the amount of hot  
30 draw, the higher the tenacity.

To further understand the invention reference will be made to the attached drawing that forms part of the present application.

35 The drawing is a side elevational view partly in section showing schematically an apparatus arrangement of a type which can be used in carrying out the process of the present invention;

40 Referring now to the drawing, a water coagulable solution comprising a polyvinyl ester of a halogenated acetic acid dissolved in an organic oxygen-containing liquid is passed under pressure from a supply tank (not shown) through a conduit and thence through a filter  
45 pump wherein undissolved particles and foreign materials in the solution are removed.

The solution then passes to a spinneret suitably disposed below the upper surface of coagulating liquid composed primarily of water and contained in an open top spinning trough or bath. The solution may be extruded through a single orifice or a plurality of orifices in the spinnerette to form a filament or bundle of filaments. The extruded streams of polymer are directed through the liquid for a predetermined and sufficient distance to cause the solution to coagulate as desired. A guide may be employed to define the path taken by the filaments in the bath. Fresh liquid is continuously supplied to the bath through the pipes placed near the bottom of each end of the bath.

The coagulated filaments are withdrawn by means of a positively driven take up roller or thread advancing means, the peripheral speed of which preferably is synchronized with the extrusion speed so that the filaments during their travel between the spinnerette and the rollers may be attenuated and if desired attenuated up to the point just short of where filamentary breakage occurs. After passing around the take up roller the filaments are directed into a second spinning trough or bath containing boiling water. The filaments are then directed around hydrolysis rollers which are partially submerged in the hydrolysis bath. After hydrolysis the fibers are passed over drier rollers. At this point the filaments may be taken up on a winder and later hot drawn if desired or directed on to the first hot draw roller, then over a hot pin, then over second hot draw roller. Finally, the fibers are taken up on a cone winder.

The relationship of drawing variables to the ultimate fiber tenacities obtained by the spinning process just described is noteworthy because a number of widely varying drawing combinations may be used to obtain fibers having tenacities higher than 9 grams per denier. Typical variations are found in Table I.

TABLE I

## DRAWING COMBINATIONS

Sample	Pre Hydrolysis Stretch* Draw Ratio	Post Hydrolysis Stretch Draw Ratio	Hot-Draw Stretch Draw Ratio	Total Stretch Draw Ratio	Tenacity of Yarn (gm/den.)
1	4.2	1.0	2.0	8.4	10.1
	2.3	2.7	1.2	7.5	10.5
2	2.3	2.7	1.5	9.3	11.7
3	2.3	2.7	2.1	10.3	13.7
4	1.2	2.6	1.8	5.6	11.6

\* Does not include jet-stretch.

Two specific requirements have been determined. First the hot draw step is necessary for high tenacity and the jet stretch, the stretch imparted to the fiber between the spinnerette face and the take up roller, has to be kept very low. For high tenacity fibers, i.e. fibers having tenacities of 9 grams per denier or above, a total stretch (exclusive of jet stretch) of about 7 to 11 stretch ratio is generally required. Little difference is noted whether the fiber is highly stretched, up to a draw ratio of 5, or only slightly stretched, at a draw ratio of about 1.2, before it is hydrolyzed. Characteristic tensile properties of the high strength and low strength stereoregular polyvinyl alcohol fibers of this invention are shown in Table II.

TABLE II

## PHYSICAL PROPERTIES OF PVA FIBERS

	High Strength Fibers	Low Strength Fibers
Denier (d.p.f.)	1—5	2—15
Tenacity (gm/den)	9.0—13.7	1.5—6.0
Elongation (%)	4—20	15—70
Modulus gm./den	74—225	20—200

The highest average tenacity obtained was 13.7 grams per denier. Tenacities of 9 to 11 grams per denier are obtained without undue difficulties. Polymers from different polymerizations give equally good fibers; samples 1 to 4 of Table I all were from different polymerization runs.

Characteristically, and as would be expected, low elongation often accompanied high tenacity. The ease, however, with which it is possible to obtain elongations below 7 percent was surprising. Elongations as low as 4 percent were obtained.

Another surprising feature of this invention is the great loss in fiber weight which is so easily tolerated by the fiber, and yet results in a fiber having very excellent tensile properties. In the conversion of polyvinyl trifluoroacetate to polyvinyl alcohol, the theoretical weight loss is 69 percent. Thus, over two-thirds of the original weight of the spun fiber is lost in the hydrolysis step.

The effect of polymer molecular weight on the spinning process and the properties of the resultant fibers is not noticeable within the range of usual spinning viscosities. No

noticeable differences were observed in the spinnability of polymers having intrinsic viscosities within the range of 0.57 to 0.9, nor were significant differences observed in ultimate fiber properties obtained.

5 In the case of polymers of lower molecular weight ranges, solutions containing up to about 38 percent by weight of polymer may be spun whereas in the case of higher molecular weight polymer the concentration of polymer in the spinning solution was necessarily lower. This factor strongly favors the use of lower molecular weight polymer to produce fibers having the ultimate in desirable properties.

7 The fibers of this invention exhibit good hot wet properties. High strength fibers that have been relaxed in boiling water actually show about the same tenacity in water at 20 70° F. or when measured at standard conditions. In some cases they were actually stronger in water at 70° F. Even in the case of quite low tenacity fiber, the differences in the elongations and tenacities of fiber in water at 25 70° F. and those measured at standard conditions for "boiled off" fiber were small. In water at 200° F. high tenacity fibers usually retained about 60 percent of their original tenacity and about 70 percent of their 30 "boiled off" tenacity with elongations usually ranging from 10 to 20 percent. The boiling water shrinkage of these fibers varied greatly with the tenacity of the fiber. It reached a minimum value of around 5 percent for 35 high tenacity fibers. The moisture regain also increased with decreasing tenacity, the values ranged from about 5 percent to 9 percent at 65 percent R.H.

40 In general, the fibers of this invention may be characterized as having very high strength, up to 14 grams per denier tenacity, with tenacities in the range of 9 to 13 grams per denier tenacity being readily obtained. Very low elongations at high strength are possible but, on the other hand, the fibers can be prepared with normal tenacity and elongation. 45 They have good hot wet properties, light

stability is better than nylon 66. Good growth properties, high fiber modulus, good heat stability and excellent knot strength are other characteristic features of the fibers of this invention.

The fibers of this invention are useful in a wide variety of commercial center or industrial and other uses. In the form of fibers and filaments, they may be used as filters, industrial belting reinforcement in laminates and plastics, apparel and tire cord.

The invention is further illustrated by the following examples in which all parts and percentages are by weight unless otherwise indicated.

#### EXAMPLE I

A 15 gram portion of stereoregular polyvinyl trifluoroacetate was dissolved in 85 grams of acetone which had been dried over anhydrous sodium sulfate to give a clear, colorless, viscous solution containing 15 percent solids. The polyvinyl trifluoroacetate had an intrinsic viscosity of 2.75 as measured in methyl ethyl ketone at 25° C.

For the spinning of this solution a conventional wet spinning machine was used. The solution was wet spun through a 10 hole spinneret into a bath of water at room temperature. The coagulated fiber was run over 1 set of godets, then to a second set on which the fiber was wrapped 20 times. The fiber on this set of godets was allowed to remain for approximately 2 minutes while the godets rotated in a pan of ammonium hydroxide (28 percent  $\text{NH}_3$ ). The fiber was hydrolyzed continuously to stereoregular polyvinyl alcohol fiber during the 2 minute period. Then the fiber was passed over a set of steam heated drying rolls and on to a take up spool. A portion of the fiber was machine drawn across a hot pin at 190° C. with an almost maximum stretch which resulted in an increase in length of approximately 60 percent. Infrared examination of the fiber showed that it was essentially completely hydrolyzed. Single filament testing of the fiber was conducted and the results are shown below in tabular form.

TABLE III  
DATA FOR FILAMENTS DRAWN OVER A HOT PIN

	Standard Conditions		70° F. in	200° F. in
	Unboiled Fiber	Boiled Fiber (relaxed)	Water Boiled Fiber	Water Boiled Fiber
	21 breaks	17 breaks	19 breaks	15 breaks
Denier	2.41	2.31	2.49	2.48
Tenacity g/d	7.85	8.18	7.33	4.41
Elongation (%)	7	12	13	16

Boiling Water Shrinkage = 5.3%

#### EXAMPLE II

To a 206 gram portion of stereoregular polyvinyl trifluoroacetate there was added 352 grams of dry acetone. The ingredients were mixed thoroughly, heated to 32° C., and agitated for 2 hours to produce a clear solution with a viscosity of about 1200 centipoises. The solution was extruded at a temperature of 23° C. through a conventional spinneret into a water coagulation bath, the fibers were continuously withdrawn from the bath using a jet stretch of 0.24, and then were stretched 2.3 times their length in a boiling water bath. Continuous hydrolysis was accomplished using two godets and ammonium hydroxide as in Example I. After hydrolysis the resulting

polyvinyl alcohol filaments were stretched 2.7 times while wet, dried on rollers heated to 80° C. then drawn 2.1 times over a heated draw pin at 150° C. The filaments had a a denier of 1.3, an average tenacity of 13.7 grams per denier, with individual breaks over 15 gpd., and an elongation of 6 percent.

#### EXAMPLE III

A series of spinnings were conducted to determine the versatility of the hot stretch step of the spinning process for high and low tenacity fibers. All samples were spun according to Example I and the results are tabulated below.

TABLE IV

Sample	Hot Stretch Ratio	Pin Temp. °C.	Tenacity g/d	Elongation
1	1.8	150	11.6	10
2	2.1	150	9.0	5.5
3	2.0	140	10.0	6
4	maximum	150	7.0	7
5	none	—	1.7	34
6	none	—	1.4	20
7	none	—	3.2	38

This data shows that the hot stretch is necessary in order to obtain high tenacity fibers.

WHAT WE CLAIM IS:—

- 5 1. A process for the preparation of boiling-water insoluble, stereoregular polyvinyl alcohol fibers or filaments, comprising wet or dry spinning a solution of a stereoregular polyvinyl ester of halogenated acetic acid, in which
  - 10 all three hydrogen atoms of the methyl group in the acetic acid have been substituted by either chlorine, fluorine or by both chlorine and fluorine, and continuously hydrolyzing the resulting filaments.
- 15 2. The process according to Claim 1, comprising the steps of:
  - (a) extruding a solution of a stereoregular polyvinyl ester of a halogenated acetic acid into a coagulation medium,
  - 20 (b) stretching the resulting filaments,
  - (c) continuously hydrolyzing the filaments,
  - (d) drying the filaments, and
  - (e) hot drawing the filaments.
- 25 3. The process according to Claim 1, comprising the steps of:
  - (a) extruding a solution of from 12 to 40 percent by weight concentration of a stereoregular polyvinyl ester of a halogenated acetic acid dissolved in an organic oxygen-containing liquid into a coagulation bath containing a liquid which is a non-solvent for the polymer,
  - 30 (b) stretching the resulting filaments,
  - 35 (c) continuously hydrolyzing the filaments,
  - (d) stretching the filaments immediately after hydrolysis,
  - (e) drying the filaments by passing said filaments over a heated surface, and
  - 40 (f) hot drawing the filaments.
4. The process according to Claim 1, comprising the steps of:
  - (a) extruding a solution of a stereoregular polyvinyl ester of a halogenated acetic acid dissolved in an organic oxygen-containing liquid into a coagulation bath containing a liquid which is a non-solvent for the polymer,
  - 45 (b) stretching the resulting filaments at a draw ratio of from 1.05 to 8.0:1.0 in a hot aqueous bath,
  - 50 (c) hydrolyzing the filaments continuously with a hydrolysis agent which is a base having a  $pK_b$  value (as hereinbefore defined) less than 8.0,
  - 55 (d) stretching the filaments immediately after hydrolysis,
  - (e) drying the filaments by passing said filaments over a heated roller at a temperature of from 80° C. to 110° C.,
  - 60 (f) and drawing the filament over a heated surface while subjecting said filament to a stretch at draw ratio of from 1.1 to 5.0:1.0.
5. The process according to Claim 3, wherein the organic oxygen-containing liquid is any one of the following:—acetone, methylethyl ketone, tetrahydrofuran or dimethylacetamide.
6. The process according to Claim 3, wherein the hydrolysis agent is any one of the following:— ammonium hydroxide, methanolic ammonia, tetramethyl ammonium hydroxide, a primary amine or a secondary amine.
7. The process according to Claim 1, comprising the steps of:
  - (a) extruding a solution of from 12 to 40 percent by weight concentration of vinyl trifluoroacetate dissolved in acetone into a coagulation bath comprising water,
  - 80 (b) stretching the resulting filament at a draw ratio of from 1.05 to 8.0:1 in a boiling water bath,
  - 85 (c) continuously hydrolyzing the filament with ammonium hydroxide for a period of time of from 1—3 minutes,
  - (d) stretching the filament immediately after hydrolysis,
  - 90 (e) drying the filament by passing said filament over a heated roller at a temperature of from 80° C. to 110° C.
  - 95 (f) and drawing the filament over a heated surface while subjecting said filament to stretching at a draw ratio of from 1.1 to 5.0:1.0.
8. The process according to Claim 7, wherein the stereoregular polyvinyl ester of a halogenated acetic acid is vinyl chlorodifluoroacetate.
9. A process for the preparation of boiling-water insoluble stereoregular polyvinyl alcohol filaments substantially as hereinbefore described with reference to the Examples.
10. A process for the preparation of boiling-water insoluble stereoregular polyvinyl alcohol filaments substantially as hereinbefore described with reference to the accompanying drawing.
11. Stereoregular polyvinyl alcohol filaments when produced by the process claimed in any one of the preceding claims.

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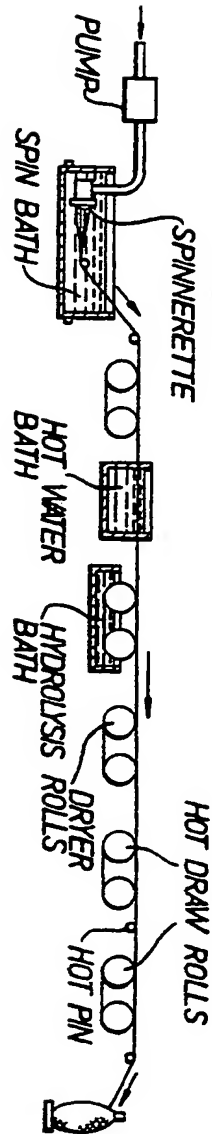


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COMPLETE SPECIFICATION

1 SHEET

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